a solution of freshly distilled 5-(β -chloroethyl)-4-methylthiazole¹⁶ (3.2 g, 0.02 mol) in acetone (analytical grade, 10 mL) at room temperature. The reaction mixture was subsequently kept at ≈ 20 "C for 24 h. After storage of the reaction mixture in the refrigerator for 1-2 h, a white precipitate was formed. This was collected and washed with acetone (25 mL) to afford the white crystalline product: yield 4.9 g (85%); mp 92 °C; ¹H NMR (200 MHz, D₂O) δ 2.57 (s, 3, C₄-CH₃), 3.48 (t, 2, *J* = 7 Hz, C₅-CH₂), 3.72 (s, 3, CH₃O), Anal. Calcd for C₈H₁₄ClNO₄S₂: C, 33.39; H, 4.90; N, 4.87; S, 22.28. Found: C, 33.31; H, 5.03; N, 4.84; S, 22.40. 3.93 (t, 2, $J = 7$ Hz, CH₂Cl), 4.17 (s, 3, NCH₃), 9.78 (s, 1, C₂-H).

5-(β -Chloroethyl)-2,3,4-trimethylthiazolium Methyl Sulfate (5b). The same procedure as for 5a was used by starting from $5-(\beta$ -chloroethyl)-2,4-dimethylthiazole¹⁷ (0.88 g, 0.005 mol) and dimethyl sulfate (0.63 g, 0.005 mol) in acetone ($\overline{3}$ mL). After evaporation of the solvent, the product was obtained as an oil which was used without purification: ${}^{1}H$ NMR (200 MHz, D₂O) C_5 -CH₂), 3.71 (s, 3, CH₃O), 3.86 (t, 2, $J = 6$ Hz, CH₂Cl), 3.92 (s, δ 2.49 (s, 3, C₄-CH₃), 2.92 (s, 3, C₂-CH₃), 3.38 (t, 2, J = 6 Hz, 3 , NCH₃).

5-(yChloropropyl)-3,4-dimethylthiazolium Methyl Sulfate (7). The same procedure as for 5a was used by starting from **5-(y-chloropropyl)-4-methylthiazole18** (3.4 g, 0.019 mol) and dimethyl sulfate (2.4 g, 0.019 mol) in acetone (10 mL). After evaporation of the solvent, the product was obtained as an oil which was used without purification: ¹H NMR (200 MHz, D₂O) δ 2.17 (m, 2, J = 7 Hz, CCH₂C), 2.51 (s, 3, C₄-CH₃), 3.13 (t, 2, J $=$ 7-8 Hz, C₅-CH₂), 3.66 (t, 2, $J = 6$ Hz, CH₂Cl), 3.73 (s, 3, CH₃O), C, 35.82; H, 5.34; N, 4.64; S, 21.25. Found: C, 35.34; H, 5.57; N, 4.56; S, 20.71. 4.11 **(s, 3, NCH₃)**, 9.68 **(s, 1, C₂-H)**. Anal. Calcd for $C_9H_{16}CINO_4S_2$:

N-Methyl-N-[**(2)-1-(2-thietanylidene)ethyl]formamide** (6a). Compound 5a (2.9 g, 0.01 mol) was dissolved in water (10 mL) at room temperature, and trichloroethylene (10 mL) was added. The water phase was separated after extraction and a new portion of trichloroethylene (10 mL) was added followed by 1 M sodium hydroxide (22 mL, ≈ 0.022 mol) in one portion. After the two-phase system was stirred for 5-10 min at ambient temperature, the phases were separated, and the water phase was extracted with trichloroethylene (10 mL). The combined organic

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de Laire Chimie SA, 62104 Calais, France.

phases were dried (Na_2SO_4) and evaporated. Distillation afforded the product as a colorless oil: yield 1.2 g (78%); bp 71-73.5 \textdegree C (0.05 mmHg) ; n^{25} _D 1.5514; IR (neat) 1670 cm⁻¹ (amide C=0); ¹H $(m, 2, C=CH_2)$, 8.02 (s, 1, CHO); ¹³C NMR (CDCl₃) δ 15.0, 20.6, 28.7, 34.2, 124.3, 129.3, 162.419; mass spectrum, *m/z* (relative intensity) $157 \ (42, M^+), 124 \ (66), 116 \ (43), 111 \ (84), 68 \ (37), 56$ (100). Anal. Calcd for $C_7H_{11}NOS: C$, 53.47; H, 7.05; S, 20.39. Found: C, 53.18; H, 6.93; S, 20.10. NMR (200 MHz, CDCl₃) *δ* 1.72 (t, 3, *J* = 1.5 Hz, = CCH₃), 2.91 (d, 3, NCH₃), 3.15–3.22 (2 t, 2 H, $J = 6$ –7 Hz, SCH₂), 3.47–3.55

N-Methyl-N-[**(2)-1-(2-thietanylidene)ethyl]acetamide** (6b). The same procedure as for 6a was used by starting from 5b (0.91 g, 0.003 mol) dissolved in water (5 mL), trichloroethylene (5 mL), and 1 M NaOH (7 **mL,** 4.007 mol). Distillation afforded the product as a colorless oil: yield 0.29 g (56%); bp 65-67 $^{\circ}$ C (0.05 mmHg) ; IR (neat) 1655 cm⁻¹ (amide C=O); ¹H NMR (200) MHz, CDCl₃) δ 1.70 (s, 3, = CCH₃), 2.04 (s, 3, CH₃CO), 2.91 (s, 3, NCH₃), 3.17 (t, 2, $J = 6-7$ Hz, SCH₂), 3.48 (t, 2, $J = 6$ Hz, =CCH2); 13C NMR (CDClJ *6* 14.6, 20.3, 20.8, 31.5, 34.0, 126.6, 132.4, 170.4; mass spectrum, m/z (relative intensity) 171 (23, M⁺), 138 (54), 125 (78), 124 (14), 110 (12), 100 (22), 95 (24), 94 (ll), 82 (28), 56 (100). Anal. Calcd for C₈H₁₃NOS: C, 56.11; H, 7.65; S, 18.72. Found: C, 55.57; H, 7.74; S, 18.60.

N-[*(2)-* **l-(Dihydro-2(3H)-thienylidene)ethylI-N**methylformamide (8). The same procedure as for 6a was used by starting from 7 (3.0 g, 0.01 mol) dissolved in water (10 mL), trichloroethylene (10 mL), and 1 M NaOH (22 mL, ≈ 0.022 mol). Recrystallization from hexane-methanol afforded the product as white crystals: yield 1.6 g (92%); mp 50-52 °C; IR (CHCl₃) 1665 cm-' (amide C=O); 'H NMR (200 MHz, CDC13) 6 **1.89** (s, 3, $=$ CCH₃), 2.15 (m, 2, *J* = 6–7 Hz, CCH₂C), 2.61 (t, 2, *J* = 6–7 Hz, 141.3, 163.1; mass spectrum, m/z (relative intensity) 171 (78, M⁺), 143 (lo), 142 (16), 130 (45), 124 (65), 115 (lo), 114 (16), 112 (26), 111 (18), 110 (lo), 109 (lo), 87 (lo), 82 (19), 71 (lo), 59 (lo), 58 (12), 56 (100). Anal. Calcd for C₈H₁₃NOS: C, 56.11; H, 7.65; S, 18.72. Found: C, 56.12; H, 7.72; S, 18.72. $SCH₂$), 2.94 (s, 3, NCH₃), 3.01 (t, 2, $J = 6$ Hz, =CCH₂), 8.01 (s, 1, CHO); 13C NMR (CDC13) 6 18.7, 28.3, 30.6, 33.4, 33.7, 122.5,

Registry **No.** 5a methyl sulfate, 78919-46-7; 5b methylsulfate, 78891-19-7; 6a, 71114-46-0; 6b, 78891-20-0; **7** methylsulfate, 78891- 22-2; 8, 78891-23-3; dimethyl sulfate, 77-78-1; 5-(@-chloroethyl)-4 methylthiazole, 533-45-9; 5-(β-chhloroethyl)-2,4-dimethylthiazole, 31299-90-8; **5-(y-chloropropyl)-4-methylthiazole,** 6469-36-9.

(19) For assignment of 13C NMR signals of compound **6a, see** ref 4a.

Amidoselenation of Olefins and Its Utilization for Synthesis of Allylic Amides

Akio Toshimitsu, Toshiaki Aoai, Hiroto Owada, Sakae Uemura,* and Masaya Okano

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Received July 3, 1981

The reaction of phenylselenyl chloride with olefins in acetonitrile containing trifluoromethanesulfonic acid and water affords β -acetamidoalkyl phenyl selenides in good to excellent yields. This represents the first example of one-pot amidoselenation of mono- and disubstituted olefins. The reaction can be carried out in benzonitrile, propionitrile, butyronitrile, or ethyl cyanoacetate. It was confirmed that the amidoselenation reaction proceeds with trans stereospecificity. Oxidative elimination of the produced β -amidoalkyl phenyl selenides gives allylic amides selectively in good to excellent yields. These two reactions constitute a good method for conversion of olefins to allylic amides.

The chemistry of organoselenium compounds is of current interest owing to their fertile and easily manipulated nature.¹ For utilization in organic syntheses, one of the key reactions is the introduction of selenium into

⁽¹⁶⁾ This compound was obtained from A. B. Astra, 15185 Sdertiilje, Sweden.

Table I. Reaction Conditions **for** Amidoselenation of Cyclohexene *^a*

 a^a Cyclohexene (1 mmol) and CH₃CN (6 mL) at reflux temperature.

^a Cyclohexene (1 mmol) and CH₃CN (6 mL) at reflux temperature. ^P Determined by liquid chromatography.
PhSeSePh (0.5 mmol) and Br₂ or SO₂Cl₂ (0.5 mmol). ^P At room temperature. ^P p-Toluenesulfonic acid mon At room temperature. *e* p-Toluenesulfonic acid monohydrate. *f* Only 0.1 mmol added in this case.

organic molecules. Electrophilic addition of the phenylseleno group to olefins is one of the valuable methods and has many precedents in the case of the oxyselenation re-
action.^{2,3} In view of the important role of nitrogen In view of the important role of nitrogen functional groups in biologically active compounds, the introduction of both phenylseleno and nitrogen functional groups to olefins-aminoselenation of olefins-should provide a valuable method for synthetic strategies. We have now found that the reaction of phenylselenyl chloride with olefins in acetonitrile containing trifluoromethanesulfonic acid and water affords β -acetamido selenides in good to excellent yield^.^ Although several methods have been reported which result in the aminoselenation of olefins, some of them⁵ require two-pot reactions and/or the preparation of effective selenium reagents, and others⁶ can only be applied to special type of olefins such as ole-

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finic urethanes or Michael acceptors. Our procedure gives better yields and the reaction is simpler and more general.

Double bond formation by oxidative elimination of the phenylseleno group constitutes another key reaction for organic syntheses using organoselenium compounds. The direction of the elimination is well established for the alkyl aryl selenides bearing a heteroatom such **as** oxygen,' sulfur,⁸ or chlorine^{7b,9} at the β -position of the alkyl group. However, little is known for the selenides bearing a nitrogen functional group at the β -position. It has only been reported that in the oxidation of β -(dimethylamino)alkyl phenyl selenides^{6a} an elimination away from the dimethylamino group leading to allylic amines is moderately favored and that a mixture of allyl azide and vinyl azide (isomer ratio 3:2) is formed by oxidation of β -azidocyclohexyl phenyl selenide. 5b,10 We have now found that oxidative elimination of the produced β -amidoalkyl phenyl selenides gives allylic amides selectively in good to excellent yields.¹¹ These two reactions constitute a good method for conversion of olefins to allylic amides.¹² We describe here the details of these reactions as one of our series of studies on organoselenium chemistry. $3,13$

Results and Discussion

Amidoselenation. In a typical reaction, trifluoromethanesulfonic acid (1 equiv) and water *(5* equiv) were added to a solution of the adduct of cyclohexene and phenylselenyl chloride in acetonitrile at room temperature, and the resulting solution was stirred under reflux for 1 h to give **trans-2-acetamidocyclohexyl** phenyl selenide **(1,** $R = CH₃$) almost quantitatively (eq 1). The reaction conditions examined are summarized in Table I. The yield of 1 ($R = CH₃$) was not satisfactory when either acid or water was omitted (entries *5* and 6). Among several

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organic and inorganic acids examined, trifluoromethanesulfonic acid was found to be most effective (entries 1, 9, 10, and 11). This reaction also proceeded smoothly when phenylselenyl halides were prepared in situ by the reaction of diphenyl diselenide with bromine or sulfuryl chloride, indicating that in the latter case the produced sulfur dioxide did not interfere with this reaction (entries 3 and **4).14** When the amount of water was reduced to 1 molar equiv with respect to the substrates, the yield of $1 (R =$ $CH₃$) was slightly lowered, while 1 (R = $CH₃$) was produced only in a yield of 30% when the amount of trifluoromethanesulfonic acid was reduced to 0.1 molar equiv with respect to the substrates. The reaction also proceeded at room temperature, but the yield of 1 ($R = \tilde{C}H_3$) was not satisfactory even with a prolonged reaction time. This reaction is reminiscent of the Ritter amide synthesis and related reactions.¹⁵ As shown in eq 2, this reaction seems

to proceed by the attack of the nitrogen atom of acetonitrile on the episelenonium ion (which exists in equilibrium with the adduct) to give the intermediate **2,** which \leq CH₃). It should be worth noting that although phenylselenyl chloride in acetonitrile-water **(5:l)** is a good reagent for hydroxyselenation of olefins,^{3f} none of β -hydroxyalkyl phenyl selenide was detected in the products under the present reaction conditions. This seems to be due to the difference of the amount of water (ratio of ca. **1/67)** and also to the presence of acid which can associate with water.

From other cyclic olefins such as cyclopentene, cycloheptene, and cyclooctene, β -amido selenides $3-5$ were obtained in moderate to good yields (eq **3).**

When this reaction was applied to linear terminal olefins, a phenylseleno group was introduced on the terminal

Table **11.** Amidoselenation of Representative Olefins **a**

olefin	time, h	product(s)	yield, $\frac{b}{b}$ % (isomer ratio) ^c
cyclopentene	1	3	67
cyclohexene	1	$1 (R = CH_2)$	98
cycloheptene	1	4	55
cyclooctene	1	5	42
1-hexene	3	$6 + 7$ (R = $n\text{-}C_{\text{-}}H_{\text{-}}$	79 (84:16 6/7)
1-octene	3	$6 + 7$ (R = $n\text{-}C_{\epsilon}H_{\infty}$	67 (85:15 6/7)
1-decene	3	$6 + 7$ (R = $n\text{-}C_{\bullet}H_{\bullet}$	77 (88:12 6/7)
1-dodecene	1	$6 + 7$ (R =	68 (86:14 6/7)
1-hexadecene	3	$n\text{-C}_{10}H_{21}$ $6 + 7 (R =$	64 (87:13 6/7)
1-octadecene	3	$n\text{-}C_{14}H_{29}$ $6 + 7 (R =$ $n-C_{16}H_{33}$	65 (86:14 6/7)
styrene	6	6 ($R = Ph$)	36
trans-2-butene	1	$ervthro-8$	70
cis-2-butene	1	$threeo-8$	74
<i>cis-2-octene</i>	3	$9+10$	89 (46:54 9/10)

 a Olefin (5 mmol), PhSeCl (5 mmol), $CF₃SO₃H$ (5 mmol), H,O **(25** mmol), and CH,CN (30 mL) at reflux temperature. ^b Isolated yield. ^c Determined by liquid chromatography.

carbon atom to give **6** predominantly, but a small amount of regioisomer **7** was also obtained **(6/7** ratio of ca. 6; eq **4).** If desired, each isomer can be isolated in a pure form

$$
RCH = CH2 \frac{Phsec1/CH3CN}{CF3SO3H/H2O}
$$

$$
RCHCH2SePh + RCHCH2NHCOCH3(4)
$$

by column chromatography (see Table VI). Although the reaction mixture was heterogeneous in the cases of hexadecene and octadecene, the yields and isomer ratios were almost the same as those in homogeneous reactions. In the case of styrene, a phenylseleno group was introduced selectively into the terminal carbon atom to give only **6** $(R = Ph)$ in a 36% yield, several attempts to improve the yield being unsuccessful.

We investigated the stereochemical course of the reaction using *cis-* and trans-2-butenes **as** olefinic substrates. A different stereoisomer (threo or erythro) of 2-acetamido-&(phenylseleno)butane **(8)** was obtained selectively from *cis-* or trans-2-butene (eq *5).* These stereoisomers

$$
CH_{3}CH=CHCH_{3} \xrightarrow{PISECI/CH_{3}CN} CH_{3}CHCHCH_{3}
$$
\n
$$
S_{\text{ePh}}
$$
\n
$$
S_{\text{ePh}}
$$
\n
$$
S_{\text{ePh}}
$$
\n
$$
S_{\text{ePh}}
$$

$trans \rightarrow$ erythro

were well distinguished by their **'H** NMR spectra. It **was** revealed that the product obtained from cis-2-butene **was** identical with **an** authentic sample of threo-8 prepared by acetylation of known **cis-2,3-dimethylaziridine16** followed by trans ring opening^{5a} by sodium phenylselenolate. Consequently, the product obtained from trans-2-butene was determined to erythro-8. This result indicates that the amidoselenation reaction proceeds with trans stereo-

⁽¹⁴⁾ It has been reported (ref **7c,** footnote **3)** that in the case where PhSeCl is prepared in situ by the reaction of sulfuryl chloride with

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Table 111. Amidoselenation in Various Nitriles ^a

^a Cyclohexene (5 mmol), PhSeCl (5 mmol), CF₃SO₃H (5 mmol), and H₂O (25 mmol). ^b Isolated yield.

specificity as shown in eq 2. This is in accord with the report that the reaction of an episulfide with a nitrile in the presence of a strong acid proceeds with trans stereospecificity.^{15d} When cis-2-octene was treated under the same conditions, a mixture of almost equal amounts of regioisomers **9** and **10** was obtained. These isomers can

be separated easily by column chromatography. Both **9** and **10** seem to be the threo isomer **as** in the cis-2-butene case. Typical results are summarized in Table 11. When 1-methylcyclohexene or 2,3-dimethyl-2-butene was treated under the same reaction conditions, none of β -amido selenides were obtained, and several attempts with variant conditions resulted in failure.

The amidoselenation reaction can be carried out not only in acetonitrile but also in other solvent containing a cyano group such as benzonitrile, propionitrile, butyronitrile, or ethyl cyanoacetate. **As** shown in Table 111, @-amido selenides containing various substituents on the amido group were prepared in excellent yields by using cyclohexene as an olefinic substrate. In the case where ethyl cyanoacetate was used as the solvent, the formation of a side product might be expected if the episelenonium ion was attacked by the oxygen atom of the ester group^{3d,17} in ethyl cyanoacetate. However, the products obtained were β -amido selenide 1 ($R = CH_2COOCH_2CH_3$; 72% yield) and diphenyl diselenide (25% yield), none of oxyselenated products being detected. This result indicates that the attack of the nitrogen atom of cyano group on the episelenonium ion is much more favored than that of oxygen atom of ester group. The hydrolysis of the ester group under the reaction conditions seems to be very slow, as evidenced by the fact that none of ester group in β -amido selenide 1 $(R = CH_2COOCH_2CH_3)$ was hydrolyzed.

Combining the results summarized in Tables I1 and 111, it is clear that a wide range of β -amido selenides can be prepared by this one-pot amidoselenation reaction.

Synthesis **of** Allylic Amides. By oxidation of **3** with aqueous H_2O_2 (10 molar equiv) in tetrahydrofuran at $0-20$ "C, 3-acetamidocyclopentene was obtained selectively in a yield of 83% (eq 6). None of its isomers were detected

$$
CH2 = CH - CH
$$
\n
$$
CH2 = CH - CH
$$
\n
$$
CH2 = CH - CH
$$
\n
$$
CH = CH
$$

in the product (by **'H** NMR). **As** summarized in Table IV, seven- and eight-membered-ring β -amido selenides (4 and *5)* as well as linear compounds **(8)** gave allylic amides

Table IV. Synthesis of Allylic Amidesa

a **,?-Amido selenide (2 mmol), 30% aqueous H,O, (20 mmol), and THF (20 mL) at 0-20 "C. Isolated yield. By pyrolysis of isolated selenoxides (11) and with Kugelrohr distillation at 250 "C (2 torr); overall yield from 1.**

selectively in good to excellent yields under the same reaction conditions.

When six-membered-ring β -amido selenides 1 were treated under the same conditions **as** described above, none of allylic amides were formed, and, instead, white solids were obtained which were characterized as the corresponding selenoxides (11, eq 7). This result shows that

in spite of the presence of three β -protons, the selenoxides **11** do not decompose in tetrahydrofuran at 20 **"C** for 2 h. Furthermore, the isolated selenoxides 11 can be stored almost infinitely at room temperature. The stability of 11 seems to be due to the formation of an intramolecular hydrogen bond between the hydrogen atom of amido group and the oxygen atom of the selenoxide **as** depicted in eq 7.lS This hypothesis is well supported by spectroscopic data as follows. Thus, in 'H **NMR** spectra NH protons are shielded by 2.3-2.8 ppm by the formation of selenoxide.

⁽¹⁷⁾ Garratt, D. G.; Ryan, M. D.; **Beaulieu,** P. **L.** *J. Org. Chen.* **1980,** 45, **839-845.**

⁽¹⁸⁾ Formation of an intramolecular hydrogen bond has been proposed
in 2-hydroxycyclohexyl phenyl selenoxides: Detty, M. R. J. Org. Chem.
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Table **V.** Reduction of @-Amido Selenides *a*

β -amido selenide	tin reagent (mmol)	time, h	product	vield. 6%
$1 (R = CH_1)$	$Ph_{3}SnH(2.5)$		C.H., NHCOCH,	100
$1 (R = CH_2)$	$n-Bu_3SnH(1.5)$	35	C.H., NHCOCH,	35
	Ph ₃ SnH(2)		C.H. NHCOCH,	100
6 (R = n -C ₄ H _a)	$Ph_{2}SnH(2)$		$n\text{-}C_{4}H_{2}C(NHCOCH_{3})HCH_{3}$	86
$threeo-8$	$Ph_{2}SnH(2)$		CH, C(NHCOCH,)HCH, CH,	80

 $a \beta$ -Amido selenide (0.5 mmol) and toluene (10 mL) at reflux temperature. b Determined by GLC.

In IR spectra of the selenoxides, the absorptions due to the carbonyl group were observed at a $13-27$ cm⁻¹ higher frequency than those of the corresponding selenides, which is ascribed to the dissociation of intermolecular hydrogen bond of two amide groups in **1,** i.e., I, by the formation of

> $N \left(\frac{H^{2} - 1 - 0}{C} \right) = C \left(\frac{1}{\sqrt{2}} \right)$ I

an intramolecular hydrogen bond in **11.** The IR absorptions due to N-H stretching moved to a lower frequency by $100-200$ cm⁻¹ on the formation of selenoxides. This value represents the sum of the effects of the formation of the intramolecular hydrogen bond and the dissociation described above. The measurement of ${}^{1}H$ NMR coupling constants of methine protons of **11** revealed that both substituents bear the equatorial position of cyclohexane framework. The proper dihedral angle of the C-Se and C-N bonds in a stable conformer seems to be important for the formation of an intramolecular hydrogen bond, since selenoxides were not isolated from non-six-membered-ring or linear β -amido selenides. Observation of two signals of singlet acetyl protons (2.01, 2.06 ppm; ca. 2:l) in the ¹H NMR spectrum of 11 $(R = CH_3)$ suggests that 11 $(R = CH_3)$ consists of two diastereoisomers due to the configuration on selenium in a ratio of ca. 2:1. Selenoxide fragmentation of 11 $(R = CH_3)$ in boiling tetrahydrofuran (for 1 h) or p-xylene (for 3 h) produced 3-acetamidocyclohexene selectively, but only in moderate yields (43% and 63%, respectively). The yields of allylic amides were improved without loss of selectivity by pyrolysis of **11** using Kugelrohr distillation **(250** "C, 2 torr; Table IV).

Oxidation of β -amido selenides bearing a phenylseleno group on the terminal carbon atom gave the corresponding selenoxides in almost quantitative yields, but the attempted pyrolysis of selenoxides using Kugelrohr distillation (250 \degree C, 2 torr) resulted in the formation of resinous products which could not be characterized.

As a conclusion, sequential procedures (amidoselenation of olefins and oxidative elimination) constitute a good method for the conversion of internal olefins to allylic amides bearing various substituents on the amide group.

Reduction of β **-Amido Selenides.** Finally, we describe briefly the results of the displacement of a phenylseleno group in the produced β -amido selenides with hydrogen by a recently reported method.¹⁹ By the reaction with triphenyltin hydride in refluxing toluene the β -amido selenides gave the corresponding aliphatic amides in excellent yields. When tri-n-butyltin hydride was used in place of triphenyltin hydride, the yield of aliphatic amide was unsatisfactory. Typical results are summarized in Table V. The overall procedures, the amidoselenation reaction and triphenyltin hydride reduction, represent a method for the conversion of olefins to aliphatic amides, formally the addition of amides to olefins.

(19) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem.* **SOC. 1980,** *102,* **4438-4447.**

Experimental Section

IR spectra were recorded with a Hitachi EPI-S2 spectrometer. 'H NMR spectra were taken with Varian EM-360 and JEOLCO JNM-PFT-100 instruments on solutions, in CDCl₃ with Me₄Si as an internal standard. GLC analyses were carried out with a Shimadzu 4CMPF apparatus by using a PEG-6000 (25%)-Shimalite column (1 m; \overline{N}_2 as carrier gas). Liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system and a Model 440 absorbance detector (at 254 nm) with a μ -Porasil (3.9 mm \times 0.3 m) column [hexane-tetrahydrofuran (2:l) as eluant]. Mass spectra were measured on a JEOL JMS-300 mass spectrometer connected to a JEOL LGC-20K gas chromatograph, equipped with a 1-m glass column packed with OV-17 **(2%)** on Chromosorb B, and a JMA-2000 data processing system. The ionization voltage was 24 eV for **all** compounds. Melting points were determined with Shimadzu MM-2 micro melting point determination apparatus and were uncorrected.

Materials. Triphenyltin hydride was prepared by reduction of commercial triphenyltin chloride with $LiAlH₄$ in diethyl ether under N_2 .²⁰ After the workup procedure as described in the literature, the evaporation of the solvent from the organic layer left a colorless oil which was used in subsequent reaction without further purification. All authentic samples of N-alkylacetamides were prepared by heating a benzene solution of the corresponding amine and acetyl chloride. All other organic and inorganic materials are commercial products. The characterization of new compounds is summarized in Table VI.

Amidoselenation of *cis-2-Butene*. General Procedure. cis-2-Butene was introduced to a dark red solution of phenylselenyl chloride (0.96 g, 5.0 mmol) in acetonitrile (30 mL) at room temperature until the color changed to pale yellow. Trifluoromethanesulfonic acid (0.75 g, 5.0 mmol) and water (0.45 g, 25 mmol) were then added, and the resulting mixture was stirred under reflux for 1 h. The reaction mixture was cooled to room temperature, saturated aqueous NaHCO_{3} (30 mL) was added, and the products were extracted with chloroform (3 **X** 20 mL). The organic layer was washed with brine and dried over MgSO4. Evaporation of the solvent in vacuo left a yellow solid which was subjected to column chromatography (silica gel) to give diphenyl diselenide [0.20 g, 0.62 mmol, 25%; hexane-chloroform (5:l) **as** eluant] and *threo-8* [1.0 g, 3.8 mmol, 75%; hexane-ethyl acetate (1:l) as eluant] as a pale brown solid. Recrystallization of this solid from hexane-chloroform (5:l) gave pure *threo-8* as white needles: IR (KBr disk) 3290, 3070, 2970, 1630, 1550, 1472, 1430, 1368, 1290, 1106, 728, 688 cm-'.

The same result was obtained when an aqueous solution of trifluoromethanesulfonic acid (molar ratio of acid/water of 1:5) used in almost all other reactions for convenience in weighing and storage.

Preparation **of** an Authentic Sample **of** *threo-8.* To a solution of **cis-2,3-dimethylaziridine** [prepared by the reported method16 using 2.2 g (9.3 mmol) of **threo-2-azido-3-iodobutane]** in ether (50 mL) was added triethylamine (1.5 g, 15 mmol) followed by the addition of acetyl chloride (1.2 g, 15 mmol) under ice-bath cooling. After the resulting white suspension was stirred for **24** h at 20 "C, the white solid was filtered off and washed with ether (3 **X** 20 mL). The ether filtrate was washed with saturated aqueous NaHCO₃ and dried over MgSO₄. Evaporation of the solvent in vacuo left a pale yellow oil which was purified by

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Table VI. Characterization of New Compounds **^a**

compd	mp, $\overline{^{\circ}C^{b}}$	chemical shifts, δ (J, Hz) ^c	IR, $\frac{d}{dm}$ cm ⁻¹
1 ($R = CH_3$)	149-150	1.0-2.3 (m, 8 H), 1.90 (s, 3 H), 3.00 (dt, 1 H, $J = 4$, 11), $3.6-4.0$ (m, 1 H), $5.3-5.6$ (br s, 1 H), 7.2-7.4 (m, 3 H), 7.5-7.7 (m, 2 H) ^e	3340, 1640
1 ($R = CH_2CH_3$)	101-102	1.15 (t, 3 H, $J = 7$), 0.9-1.9 (m, 6 H), 2.13 (q, 2 H, $J = 7$), 1.9–2.3 (m, 2 H), 3.01 (dt, 1 H, $J = 4$, 11), 3.5–4.1 (m, 1 H),	3320, 1647
$1 (R = CH2CH2CH3)$	67-68	5.5-6.0 (br d, 1 H, $J = 9$), 7.1-7.3 (m, 3 H), 7.3-7.7 (m, 2 H) 0.95 (t, 3 H, $J = 7$), 1.0-2.3 (m, 8 H), 1.66 (sextet, 2 H, $J = 7$), 2.10 (t, 2 H, $J = 7$), 3.02 (dt, 1 H, $J = 4$, 11), 3.6-4.0 (m, 1 H),	3420, 1647
1 $(R = Ph)$	133-134	5.4-5.7 (br d, 1 H, $J = 7$), 7.2-7.4 (m, 3 H), 7.5-7.7 (m, 2 H) ^e 1.0-1.9 (m, 6 H), 1.9-2.5 (m, 2 H), 3.16 (dt, 1 H, $J = 4$, 11), 3.6-4.2 (m, 1 H), 6.3-6.7 (br d, 1 H, $J = 8$), 7.0-7.8 (m, 10 H)	3380, 1633
$1 (R = CH2CO2CH2CH3)$	74-75	1.26 (t, 3 H, $J = 7$), 1.0-2.0 (m, 6 H), 2.0-2.4 (m, 2 H), 2.9-3.4 (m, 1 H), 3.22 (s, 2 H), 3.5-4.1 (m, 1 H),	3380, 1743, 1647
3	72	4.16 (q, 2 H, $J = 7$), 7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) 1.5-2.4 (m, 6 H), 1.84 (s, 3 H), 3.38 (q, 1 H, $J = 7$), 4.18 (quint, 1 H, $J = 7$), 6.5-6.8 (br d, 1 H, $J = 7$),	3350, 1640
4	107-108	7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) $1.4-2.2$ (m, 10 H), 1.89 (s, 3 H), 3.1-3.5 (m, 1 H), 3.8-4.4 (m, 1 H), 6.3-6.6 (br d, 1 H, $J = 7$),	3350, 1639
5	92-93	7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) $1.0-2.3$ (m, 12 H), 1.86 (s, 3 H), 3.2-3.6 (m, 1 H), 3.8-4.4 (m, 1 H), 6.2-6.5 (br d, 1 H, $J = 7$),	3350, 1641
6 (R = n -C ₄ H ₉)	$71 - 72$	$7.1 - 7.4$ (m, 3 H), $7.4 - 7.7$ (m, 2 H) $0.8-1.8$ (m, 9 H), 1.80 (s, 3 H), 3.08 (d, 2 H, $J = 5$), $3.9-4.4$ (m, 1 H), $5.5-5.9$ (m, 1 H),	3320, 1635
7 (R = n -C ₄ H ₉)	oil	7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) $0.7-1.7$ (m, 9 H), 1.87 (s, 3 H), $3.0-3.6$ (m, 3 H), $6.0-6.5$	3350, 1651
$6 + 7$ (R = n -C ₆ H ₁₃)	f	$(\text{br s}, 1 H), 7.1-7.4 \text{ (m, 3 H)}, 7.4-7.7 \text{ (m, 2 H)}$ $0.7-1.8$ (m, 13 H), 1.79, 1.87 (s, 3 H), 3.06 (d, 2 H, $J = 5$), 3.5-4.4 (m, 1 H), 5.8-6.2 (m, 1 H), 7.1-7.4 (m, 3 H),	3340, 1650, 1640
6 + 7 (R = n -C _s H ₁₇)	f	$7.4 - 7.7$ (m, 2 H) 0.7-1.8 (m, 17 H), 1.78, 1.86 (s, 3 H), 3.07 (d, 2 H, $J = 5$), $3.9-4.3$ (m, 1 H), $5.3-5.6$ (m, 1 H), $7.1-7.4$ (m, 3 H),	3370, 1650
6 + 7 (R = n -C ₁₀ H ₂₁)	f	$7.4 - 7.7$ (m, 2 H) 0.7-1.7 (m, 21 H), 1.79, 1.87 (s, 3 H), 3.08 (d, 2 H, $J = 5$), 3.8-4.4 (m, 1 H), 5.5-5.8 (br d, 1 H, $J = 8$), 7.1-7.4 (m, 3 H),	3390, 1652
6 + 7 (R = n -C ₁₄ H ₂₉)	f	$7.4 - 7.7$ (m, 2 H) $0.7-1.8$ (m, 29 H), 1.79, 1.87 (s, 3 H), 3.12 (d, 2 H, $J = 5$), 3.9-4.4 (m, 1 H), 5.6-5.9 (br d, 1 H, $J = 9$), 7.1-7.4	3380, 1651
6 + 7 (R = n -C ₁₆ H ₃₃)	\int	$(m, 3 H), 7.4-7.7 (m, 2 H)$ 0.7-1.7 (m, 33 H), 1.77, 1.84 (s, 3 H), 3.06 (d, 2 H, $J = 5$), $3.9-4.4$ (m, 1 H), $5.9-6.2$ (br d, 1 H, $J = 8$), $7.1-7.4$	3380, 1651
6 $(R = Ph)$	oil	$(m, 3 H), 7.4-7.7 (m, 2 H)$ 1.86 (s, 3 H), 3.27 (d, 2 H, $J = 7$), 5.0-5.5 (dt, 1 H, $J = 8, 7$) 6.4-6.8 (br d, 1 H, $J = 8$), 7.1-7.4 (m, 3 H),	3320, 1648
$erythro$ - $\!8$	oil	7.24 (s, 5 H), 7.4-7.7 (m, 2 H) 1.13 (d, 3 H, $J = 6$), 1.41 (d, 3 H, $J = 7$), 1.70 (s, 3 H), 3.57 $(dq, 1 H, J = 4, 7), 3.9-4.6$ (m, 1 H), 5.8-6.3 (m, 1 H),	3320, 1644
threo-8	$76 - 77$	7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) 1.17 (d, 3 H, $J = 7$), 1.37 (d, 3 H, $J = 7$), 1.92 (s, 3 H), 3.45 (dq, 1 H, $J = 4$, 7), $3.8-4.5$ (m, 1 H), $5.9-6.4$ (m, 1 H),	3290, 1631
9	semisolid	7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) 0.7-1.8 (m, 11 H), 1.37 (d, 3 H, $J = 7$), 1.94 (s, 3 H), 3.50 (dq, 1 H, $J = 4$, 7), $3.8-4.5$ (m, 1 H), $6.0-6.4$ (br d,	3350, 1644
10	$77 - 78$	1 H, $J = 9$), 7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) $0.7-1.9$ (m, 11 H), 1.18 (d, 3 H, $J = 7$), 1.95 (s, 3 H), $3.1-3.5$ (m, 1 H), $4.1-4.6$ (m, 1 H), $5.6-6.0$ (br d, 1 H,	3310, 1640
11 (R = CH_3)	118-120 dec	$J = 8$, 7.1-7.4 (m, 3 H), 7.4-7.7 (m, 2 H) 1.0-2.3 (m, 8 H), 2.01, 2.06 (s, 3 H, ca. 2:1), 2.98 (dt, 1 H, $J = 4, 10$, 3.6–4.1 (m, 1 H), 7.4–7.7 (m, 3 H), 7.8–8.0	3240, 1667 (816)
11 (R = $CH_2CH_2CH_3$)	131-132 dec	$(m, 2 H), 8.1-8.4$ (br d, 1 H, $J = 8$) ^e 0.95 (t, 3 H, $J = 7$), 0.8-2.2 (m, 8 H), 1.72 (sextet, 2 H, $J = 7$), 2.21 (t, 2 H, $J = 7$), 2.92 (dt, 1 H, $J = 4$, 12), 3.7-4.1 $(m, 1 H), 7.4-7.7$ $(m, 3 H), 7.7-7.9$ $(m, 1 H), 7.8-8.0$ $(m, 2H)^e$	3220, 1660 (801)
	69-70	1.94 (s, 3 H), 2.1-2.9 (m, 4 H), 4.8-5.2 (m, 1 H), 5.6-5.8 (m, 1 H , 5.9–6.2 (m, 1 H), 6.2–6.5 (m, 1 H)	3320, 1640
იამჯ≷მკ€Ha	semisolid	0.92 (t, 3 H, $J = 7$), 1.0-2.5 (m, 10 H), 4.3-4.8 (m, 1 H), 5.5–6.1 (m, 2 H), 6.4–6.8 (br d, 1 H, $J = 9$)	3350, 1642
	74–75	1.0-2.3 (m, 8 H), 1.97 (s, 3 H), 4.3-4.8 (m, 1 H), $5.3 - 6.0$ (m, 2 H), $6.5 - 7.1$ (m, 1 H)	3370, 1637

Table **VI** *(Continued)*

^a Satisfactory combustion analytical data (±0.4%) for C, H, and N were obtained. ^b After recrystallization from hexanechloroform (5-1O:l). film for oils and semisolids; v_{N-H} , $v_{C=0}$, (and $v_{Se=0}$). e_{100} MHz NMR. *I* Not determined because a pure isomer was not obtained by recrystallization from hexane-chloroform (10: 1). 60-MHz NMR unless otherwise stated. $\frac{d}{d}$ Measured on KBr disks for all crystals and on a liquid

distillation using a Kugelrohr apparatus $[\sim]140$ °C (20 torr)] to give **cis-N-acetyl-2,3-dimethylaziridine:** 0.37 g (3.3 mmol, 35%); IR (film) 3000,2950,1695,1420,1364,1300,1230 cm-'; 'H NMR δ 1.23 (d, 6 H, $J = 6$ Hz), 2.07 (s, 3 H), 2.4-2.7 (m, 2 H).

To a suspension of diphenyl diselenide (0.47 g, 1.5 mmol) in ethanol (15 **mL)** was added sodium borohydride (0.13 g, 3.3 mmol) in batches at room temperature to give a yellow solution. A solution of **cis-N-acetyl-2,3-dimethylaziridine** (0.34 g, **3.0** mmol) in ethanol *(5* **mL)** was then added, and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was poured into aqueous HCl $(0.2 \text{ N}, 50 \text{ mL})$, and the products were extracted with ether $(3 \times 40 \text{ mL})$. The organic layer was washed with saturated aqueous $NAHCO₃$ and dried over MgSO₄. Evaporation of solvent in vacuo left a yellow solid which was subjected to column chromatography (silica gel) to give diphenyl diselenide (0.084 g, 0.27 mmol, 18%; hexane as eluant) and *threo-8* [0.49 g, 1.8mmol,60%; hexane-ethyl acetate (1:2) as eluant] both as solids. Recrystallization of the latter solid from hexane-chloroform (5:l) gave white needles, mp 77-78 "C. Spectroscopic data (IR and ${}^{1}\text{H}$ NMR) of this crystal was identical with that of the β -amido selenide obtained from cis-2-butene, and the mixture melting point was not depressed.

Synthesis **of** 3-Acetamidocyclopentene by Oxidative Elimination **of** 3. General Procedure. To a solution of 3 (0.56 g, 2.0 mmol) in tetrahydrofuran (20 mL) was added 30% aqueous H_2O_2 (2.3 g, 2.0 mmol) dropwise at 0 °C, and the resulting solution was stirred at 20 °C for 2 h. The solution was poured into 1 N aqueous NaOH (100 mL), and basic products were separated from the organic layer by extraction with 0.5 N aqueous HCl (3×30) mL). The aqueous layer was rendered alkaline by addition of NaOH pellets and again extracted with chloroform (3 **X** 50 mL). After the latter organic layer was dried over $MgSO₄$, evaporation of solvent gave pure 3-acetamidocyclopentene (0.21 g, 1.7 mmol, 83%) **as** the sole product: IR (KBr disk) 3320,3090,2980,2875, 1640, 1552, 724 cm-'.

Synthesis **of** 3-Acetamidocyclooctene by Oxidative Elimination **of 5.** After the oxidation of **5** (0.65 g, 2.0 mmol) by 30% aqueous H_2O_2 (2.3 g, 20 mmol) as described above, the reaction mixture was poured into 1 N aqueous NaOH (100 mL). The products were extracted with chloroform $(3 \times 50 \text{ mL})$, and the organic layer was dried over MgSO₄. Evaporation of solvent in vacuo left a pale yellow solid which was subjected to column chromatography (silica gel) to give 3 -acetamidocyclooctene $[0.28]$ g, 1.7 mmol, *84%;* hexane-ethyl acetate (1:l) **as** eluant] as a sole product: IR (KBr disk) 3380, 3100, 3040, 2950, 2880, 1635, 1545, 760 cm^{-1} .

Isolation of Selenoxide (11; $R = CH_3$ **).** To a solution of 1 $(R = CH₃; 0.59 g, 2.0 mmol)$ in tetrahydrofuran (20 mL) was added 30% aqueous H_2O_2 (2.3 g, 20 mmol) dropwise at 0 °C, and the resulting solution was stirred at 20 °C for 2 h. The solution was poured into 1 N aqueous NaOH (100 mL) and the products were extracted with chloroform $(3 \times 50 \text{ mL})$. After the mixture was dried over MgSO₄, the solvent was removed under reduced pressure to give a pale yellow solid which was washed with ether $(3 \times 100 \text{ mL})$ to give almost pure 11 (R = CH₃): 0.60 g (1.9 mmol, 95%); white powder; IR (KBr disk) 3240,3060,2950,2870,1667, 1554,1440,1370,1309,1176,1131,967,816,749,691 cm-'. The IR spectrum of 11 ($R = CH_2CH_2CH_3$) is as follows (KBr disk): 3220, 3030, 2950, 2870, 1660, 1550, 801,750,692 cm-'.

For reference, the IR spectra of 1 $(R = CH_3)$ and 1 $(R =$ $CH_2CH_2CH_3$ are as follows: 1 $(R = CH_3)$ (KBr disk) 3340, 3060, 2930,2850,1640,1534,1437,1368,1314,1180,1110,983,744,691 cm⁻¹; 1 (R = CH₂CH₂CH₃) (KBr disk) 3420, 3080, 2950, 2880, 1647, 1533, 740, 690 cm⁻¹.

Thermal Fragmentation of 11 $(\mathbf{R} = \mathbf{C}\mathbf{H})$ **.** Pyrolysis of 11 $(R = CH₃)$ was carried out by using Kugelrohr distillation at 250 °C (2 torr). The distillate (yellow oil) was dissolved in ether (20 mL), and the basic products were extracted with 0.5 **N** aqueous $HCl (3 \times 20 \text{ mL})$. After the mixture was rendered alkaline by the addition of NaOH pellets, the aqueous layer was extracted with chloroform (3 **X** 30 mL). This organic layer was dried over MgSO,, and solvent was removed under reduced pressure to give 3-acetamidocyclohexene: 0.28 g (2.0 mmol, 100%); a pale yellow solid; mp [after recrystallization from hexane-chloroform (10.1)] $79-80$ °C (lit.^{12a} mp 78 °C).

Triphenyltin Hydride Reduction of 1 $(\mathbf{R} = \mathbf{C}\mathbf{H}_3)$ **. A ho**mogeneous toluene (10 mL) solution of 1 ($R = CH_3$; 0.148 g, 0.5 mmol) and triphenyltin hydride (0.88 g, 2.5 mmol) was heated at reflux for 4 h under stirring. The GLC analysis of the cooled solution with ethyl cinnamate (0.065 g, 0.37 mmol) as an internal standard revealed the presence of 0.50 mmol of N-cyclohexylacetamide.

Acknowledgment. We thank Dr. Kohei Tamao of Kyoto University for measurement of mass spectra.

Registry No. 1 ($R = CH_3$), 77037-14-0; 1 ($R = CH_2CH_3$), 78837-62-4; 1 (R = CH₂CH₂CH₃), 78870-20-9; 1 (R = Ph), 78837-63-5; 1 (R = CH₂CO₂CH₂CH₃), 78837-64-6; 3, 77037-13-9; 4, 78837-65-7; 5, 78837-66-8; **6** ($\overline{R} = C_4H_9$), 76570-75-7; **6** ($\overline{R} = C_6H_{13}$), 77037-09-3; **6** $(R = C_8H_{17})$, 77037-10-6; **6** ($R = C_{16}H_{23}$), 77046-78-7; **6** ($R = C_{14}H_{28}$), 78837-67-9; **6** ($R = C_{16}H_{33}$), 78837-68-0; **6** ($R = Ph$), 78837-69-1; 7 (R $= C_4C_9$, 76570-74-6; **7 (R** = C_6H_{13}), 78837-70-4; **7 (R** = C_8H_{17}), 78837-71-5; 7 ($R = C_{10}H_{21}$), 78837-72-6; 7 ($R = C_{14}H_{29}$), 78837-83-9; 08-1; **9,** 78837-74-8; 10, 78837-75-9; 11 (R = CH,), 78837-76-0; 11 **(R** 7 (R = $C_{16}H_{33}$), 78837-73-7; erythro-8, 76583-27-2; threo-8, 76587-= CH,CH,CH,), 78837-77-1; **N-2-cyclopenten-1-ylacetamide,** 78837- 78-2; **N-2-cyclohexen-l-ylbutanamide,** 78837-79-3; N-2-cyclohepten-1-ylacetamide, 78837-80-6; **N-2-cycloocten-l-ylacetamide,** 78837-81-7; **N-l-buten-3-ylacetamide,** 14001-36-6; cis-2-butene, 590-18-1; diphenyl diselenide, 1666-13-3; **cis-2,3-dimethylaziridine,** 930-19-8; **cis-N-acetyl-2,3-dimethylaziridine,** 78837-82-8; N-cyclohexylacetamide, 1124-53-4; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 1-hexene, 592-41-6; 1 octene, 111-66-0; 1-decene, 872-05-9; 1-dodecene, 112-41-4; l-hexadecene, 629-73-2; 1-octadecene, 112-88-9; styrene, 100-42-5; trans-2 butene, 624-64-6; cis-2-octene, 7642-04-8; N-cyclopentylacetamide, 25291-41-2; N-(2-hexyl)acetamide, 16538-02-6; N-(2-butyl)acetamide, 1189-05-5.